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## (54) EFFERVESCENT BLEACHING COMPOSITION

(71) We, KAO SOAP COMPANY LIMITED, a Japanese Company, of 1,1-chome, Nihonbashi-Kayabacho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an effervescent sodium percarbonate bleaching agent composition which foams vigorously and dissolves rapidly in water, and has a long shelf life.

As bleaching agents for clothing, there are known the oxygen-type and the chlorine-type bleaching agents. In Japan, chlorine-type bleaching agents which exhibit an excellent bleaching effect at a low temperature have come into general use. The chlorine-type bleaching agents are effective on cellulosic fibers but cannot be used for synthetic fibers, because they cause yellow stain damage to synthetic fibers and they decolorize dyed clothing made from synthetic fibers.

On the other hand, the oxygen-type bleaching agents have the advantages that they can be used for treating most synthetic fibers as well as cellulosic fibers, and they can be used safely for dyed clothes because of their mild bleaching action.

However, the oxygen-type bleaching agents, a typical example of which is sodium percarbonate, dissolve slowly at low temperatures and therefore a sufficient bleaching action cannot be obtained at such temperatures. Further, because of their slow dissolution, undissolved particles of the bleaching agent remain and adhere to the fibers and form local high concentration bleaching zones in which the fibers are damaged and partial decolourization is caused. Thus, the oxygen-type bleaching agents, which are effective in clothes washing at a high temperature (e.g. above 60°C) have not been used up to the present in Japan in those situations wherein washing is generally effected at a low temperature (e.g. about 20°C). In view of these circumstances, improvement in the solution velocity of oxygen-type bleaching agents has been desired.

In bleaching agents containing sodium percarbonate as an active ingredient, a so-called 'activating agent' has been incorporated to increase the bleaching power of sodium percarbonate, because of its poor bleaching power at a low temperature. However, if an activating agent is incorporated in sodium percarbonate, the stability of the sodium percarbonate is impaired seriously. Particularly, if the bleaching agent is stored for a long period of time as in domestic usage, decomposition of the sodium percarbonate occurs reducing the amount of oxygen available for bleaching, so that the composition eventually becomes unusable. Also, a caking problem occurs, and further the oxygen released by the decomposition of the sodium percarbonate can cause expansion or breakage of the container in which it is being stored.

The invention eliminates the above noted disadvantages of oxygen bleaching agents, and provides a means whereby the rate of dissolution of sodium percarbonate is improved markedly and it becomes effervescent. We have discovered that by heating sodium percarbonate at a temperature of 75 to 135°C for a period of time determined by the temperature, as will be described below, the rate of dissolution and effervescent properties of sodium percarbonate in aqueous solutions are greatly increased. This invention provides an effervescent bleaching composition having a long shelf life and a high rate of dissolution at a low temperature.

According to the invention we provide an effervescent bleaching composition comprising solid sodium percarbonate and from 5% to 200% by weight, based on the weight of the sodium percarbonate, of an activating agent therefor, wherein the sodium percarbonate has been subjected to heating at a temperature within the range 75°C to 135°C, the time

of heating being such that oxygen molecules become trapped within the solid sodium percarbonate.

Preferably, the maximum and minimum heating times at 75°C are 6 hours and 2 hours respectively, and at 135°C are 30 minutes and 5 minutes respectively, the maximum and minimum heating times at other temperatures within the range being determined by interpolation.

The amount of activating agent present is preferably from 10 to 100% by weight, based on the weight of the sodium percarbonate.

If a heating temperature below 75°C is employed, the solution velocity of the sodium percarbonate is not improved. A heating temperature above 135°C is also disadvantageous, because the bleaching power of the sodium percarbonate is reduced and the desired effervescent property substantially disappears.

Under the heating conditions specified above the reduction in the available oxygen content of the sodium percarbonate caused by the heating is 5 to 30 weight percent. When the heating time is too short, the resulting sodium percarbonate is not effervescent. On the other hand, when the heating time is too long, the effervescent property is lost, and, further the bleaching power thereof is reduced. This is considered to be owing to the conversion of a substantial proportion of the sodium percarbonate to sodium carbonate.

For a general purpose household bleaching agent, sodium percarbonate which has been heated at 100 to 110°C for about 1.5 hours is preferred.

Sodium percarbonate which has been heat treated as specified above in accordance with this invention is chemically substantially unaltered. The difference between the heat treated percarbonate and untreated percarbonate is that thought to be that the heat treated sodium percarbonate traps oxygen molecules in its crystal lattice, and these oxygen molecules are released to cause effervescence on contact with water.

The heated sodium percarbonate was analysed with Raman spectrometry, which showed that the heated sodium percarbonate has a characteristic absorption at the wave number of 1550 $cm^{-1}$ corresponding to that of oxygen molecule, but sodium percarbonate not heated was not found to have the same absorption.

In general, if non-heat-treated sodium percarbonate is stored in the form of an admixture thereof with an activating agent, the shelf life of the composition is reduced greatly, the sodium percarbonate is decomposed and the storage thereof for a long period of time is difficult. In the sodium percarbonate which has been subjected to the heat treatment, according to the invention as described above, a partial decomposition has already occurred and, therefore, it would be expected that the decomposition would be further promoted by the addition of the activating agent. However, surprisingly, the stability of the sodium percarbonate heat-treated according to the present invention is improved, and a bleaching composition having a powerful bleaching action and long shelf life can be obtained by the addition of an activating agent thereto.

This invention also provides a method of preparing an effervescent bleaching composition which comprises the step of heating solid sodium percarbonate at a temperature within the range 75°C to 135°C, the time of heating being such that oxygen molecules become trapped within the said sodium percarbonate, the solid sodium percarbonate being mixed with from 5% to 200% by weight, based on the weight of the sodium percarbonate, of an activating agent therefor, either before or after the sodium carbonate has been subjected to the said heating step.

In addition, when sodium percarbonate which has been heating according to this invention is used, no caking of the powder occurs, and excellent flow of the powder is exhibited.

The composition is preferably in particulate form.

Preferred activating agents for sodium percarbonate used in the present invention are esters of polyhydric alcohols such as glucose pentaacetate and sorbitol hexaccetate, sodium acetoxybenzene sulfonate, and N-acyl compounds such as tetraacetyl glycoluril and tetraacetyl ethylenediamine. Further, organic acid anhydrides such as succinic anhydride and phthalic anhydride can also be used. The effect of these activating agents in improving the stability of the percarbonate is not exhibited with other per compounds such as sodium perborate but rather is unique to heat-treated sodium percarbonate, prepared according to the present invention.

The bleaching composition of the present invention can be mixed, if necessary or desired, with additives such as water-soluble inorganic salts such as sodium sulfate, sodium carbonate and sodium silicate. Further, the composition can be transformed to a bleaching detergent composition by adding thereto, alone or in addition to the said salts, an anionic surfactant, nonionic surfactant or amphoteric surfactant of the type conventionally used for household clothes washing purposes.

A similar improved effect can be obtained by adding the activating agent and other optional additives to sodium percarbonate and subsequently subjecting the resulting composition to the said heat treatment at 75° to 135°C.

The proportion of heat treated percarbonate plus activating agent can be in the range of

10 to 100 percent by weight, based on the total weight of the compositions containing the additives.

The aqueous bleaching solution useful for household laundry purposes for bleaching clothes is prepared by dissolving the bleaching composition in water in an amount such that the concentration of the heat-treated sodium percarbonate is from 0.02 to 4 weight percent, based on the aqueous bleaching solution. The solution must be prepared just before its usage.

The sodium percarbonate, heat treated according to the invention, is altered by the heat treatment so as to have an improved solution velocity and effervescent property in comparison with the non-heat-treated sodium percarbonate. It has not been possible thus far to ascertain the physical and/or chemical changes that take place during the heat treatment because the instability of this compound complicates identification of various phases of the system $Na_2CO_3$—$H_2O_2$—$H_2O$.

Example 1.

The effects of various heat treatments of sodium percarbonate ($2Na_2CO_3 . 3H_2O_2$) on its solution velocity were examined.

A powdery mixture (10 to 100 Japanese standard mesh) comprising 40 parts by weight of sodium percarbonate heated at various temperatures for various periods and 10 parts by weight of glucose pentaacetate are prepared. 300 ml. of city water are placed in a 500 ml. beaker and then 3 g samples of the respective compositions are added with slow stirring at room temperature. The time required until disappearance of the particles is determined and the state of effervescence is observed. The results are given in Table 1.

TABLE 1

| Test No. | Sodium percarbonate treatment | | Solution time (sec.) | Effervescent Property |
|---|---|---|---|---|
| | Heating temp. (°C) | Heating time (hr.) | | |
| 1 | 65° | 1.5 | 240 | No effervescence |
| 2 | 80 | 1.5 | 70 | Effervescence |
| 3 | 105 | 1.5 | 15 | Vigorous effervescence |
| 4 | 130 | 1.5 | 200 | Substantially no effervescence |
| 5 | 150 | 1.5 | 240 | No effervescence |
| 6 | 80 | 4 | 20 | Vigorous foaming |
| 7 | 80 | 0.5 | 120 | Slight foaming |
| 8 | 130 | 0.17 | 15 | Vigorous foaming |
| 9 | Untreated | — | 240 | No foaming |

The sodium percarbonate which has been treated in accordance with any of tests Nos. 2, 3, 6 and 8 can be mixed with an activator in the specified proportions to produce an effervescent bleaching composition in accordance with the invention.

Example 2.

| | parts by weight |
|---|---|
| Sodium percarbonate | 45 |
| Glucose pentaacetate | 10 |
| Sodium tripolyphosphate | 30 |
| Sodium sulfate | 15 |

Bleaching agents of the above composition are prepared by using various sodium percarbonates which have not been heat-treated or which have been heat-treated under various heating conditions, and the shelf lives thereof are examined. The heat treatment is effected by placing 50 g of sodium percarbonate in a 1 liter glass beaker placed in an electrically heated constant temperature bath at 125°C for 15, 25 or 30 minutes, in accordance with the invention.

The bleaching agents are stored in a closed vessel at 40°C for 30 days. The amounts of available oxygen before the storage and after

30 days storage are measured. The shelf life can be estimated from the amount of remaining available oxygen, the results were as shown below in Table II.

TABLE II

| Sodium percarbonate (available oxygen before storage) | Amount of remaining available oxygen (% of original, after 30 days storage) |
|---|---|
| Untreated (available oxygen: 14.3%) | 82.4% |
| Heated for 15 mins. (available oxygen: 13.7%) | 93.8% |
| Heated for 25 mins. (available oxygen: 12.5%) | 95.0% |
| Heated for 30 mins. (available oxygen: 12.0%) | 95.1% |

These data illustrate that a longer shelf life is obtained by using sodium percarbonate heat treated according to the invention.

Example 3.

A powdery bleaching agent is prepared comprising 90 parts by weight of sodium percarbonates which have not been treated or which have been heat-treated under the same conditions as described in Example 2, and 10 parts by weight of tetraacetyl glycoluril as activating agent. The bleaching agent is stored in a closed vessel at 40°C for 10 days and the state of the powder after the storage and its storage stability are examined to obtain the following results given in Table III.

TABLE III

| Sodium percarbonate (available oxygen before storage) | State of Powder | Amount of remaining available oxygen (% of original) |
|---|---|---|
| Untreated (available oxygen: 14.3%) | Caking is caused | 95.2% |
| Heated for 15 mins. (available oxygen: 13.5%) | Excellent flowability | 99.2% |
| Heated for 25 mins. (available oxygen: 12.6%) | Excellent flowability | 100.0% |
| Heated for 30 mins. (available oxygen: 12.0%) | Excellent flowability | 98.5 |

Example 4.

| | |
|---|---|
| Sodium percarbonate | 30 wt. % |
| Sorbitol hexaacetate | 10 |
| Sodium tripolyphosphate | 25 |
| Sodium sulfate | 25 |
| Oxyethylene/oxypropylene block polymer (average molecular weight: about 8,000) | 10 |

A powdery bleaching agent of the above composition was prepared and stored in a sealed polyethylene bottle at room temperature. When sodium percarbonate which has been heat-treated at 105°C for 1.5 hours is used, the bleaching agent has an excellent flowability, the vessel is not expanded, and 92 percent of the available oxygen remained after 6 months storage. When non-heat-treated sodium percarbonate is used, the vessel is expanded after 3 months, the flowability of the powder is poor even if the vessel is turned upside down, and the available oxygen measured after 6 months is 28 percent.

WHAT WE CLAIM IS:—

1. An effervescent bleaching composition comprising solid sodium percarbonate and from 5% to 200% by weight, based on the weight of the sodium percarbonate, of an activating agent therefor, wherein the sodium percarbonate has been subjected to heating at a temperature within the range 75°C to 135°C, the time of heating being such that oxygen molecules become trapped within the solid sodium percarbonate.

2. A composition according to claim 1, wherein the maximum and minimum heating times at 135°C are 30 minutes and 5 minutes respectively, and at 75°C are 6 hours and 2 hours respectively.

3. A composition according to Claim 1 or 2, wherein the activating agent is glucose pentaacetate, sorbitol hexaacetate, sodium acetoxybenzene sulfonate, tetraacetyl glycoluril, tetraacetyl ethylenediamine, succinic anhydride or phthalic anhydride.

4. A composition according to any preceding Claim which is in particulate form.

5. A composition according to any preceding Claim which contains one or more of sodium sulfate, sodium carbonate, sodium silicate, an anionic surfactant, a nonionic surfactant and an amphoteric surfactant.

6. A method of preparing an effervescent bleaching composition which comprises the step of heating solid sodium percarbonate at a temperature within the range 75°C to 135°C, the time of heating being such that oxygen molecules become trapped within the solid sodium percarbonate, the solid sodium percarbonate being mixed with from 5% to 200% by weight, based on the weight of the sodium percarbonate, of an activating agent therefor, either before or after the sodium carbonate has been subjected to the said heating step.

7. A method according to Claim 6 wherein the heat treated sodium percarbonate and activated agent are also mixed with at least one additive selected from sodium sulfate, sodium carbonate, sodium silicate, anionic surfactants, nonionic surfactants and amphoteric surfactants.

8. A composition according to Claim 1 comprising 90 parts by weight of the heat-treated sodium percarbonate and 10 parts by weight of tetraacetyl glycoluril.

9. A particulate composition according to Claim 1 comprising by weight 45 parts of the heat treated sodium percarbonate, 10 parts of glucose pentaacetate, 30 parts of sodium tripolyphosphate and 15 parts of sodium sulfate.

10. A particulate composition according to Claim 1 comprising by weight 30 wt. % of the heat treated sodium percarbonate, 10 wt. % of sorbitol hexacetate, 25 wt. % of sodium tripolyphosphate, 25 wt. % of sodium sulfate, and 10 wt. % of an oxyethylene/oxypropylene block copolymer having an average molecular weight of 8000.

11. The method of Claim 6 in which the sodium percarbonate is heated to a temperature from 100° to 110°C for 1.5 hours.

12. A process for preparing an aqueous bleaching solution which comprises dissolving in water, a bleaching composition as claimed in any of claims 1 to 5 and 8 to 10 in an amount such that the concentration of said sodium percarbonate in the aqueous bleaching solution is from 0.02 to 4 weight percent, based on the weight of the solution.

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